CLAIMS

We claim:

1. A method for producing a stress-resistant heat-treated anti-reflection coated inorganic substrate comprising:

(a) coating an inorganic substrate with an inner layer comprising an oxide of titanium and an oxide of silicon;

(b) coating the inner layer with a middle layer comprising a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of silicon, nickel and transition metals of Group IIIB, Group IVB, Group VB and Group VIB of the Periodic Table;

(c) coating the middle layer with an outer layer comprising an oxide of silicon; and

(d) heat treating the coated inorganic substrate;

wherein the heat-treated anti-reflection coated inorganic substrate is resistant to cracking and crazing.

2. The method according to claim 1, wherein the inner layer has a refractive index of about 1.60 to about 1.90.

3. The method according to claim 1, wherein the middle layer has a refractive index of at least about 1.90.

4. The method according to claim 3, wherein the middle layer has a refractive index of at least about 2.0.

5. The method according to claim 1, wherein the outer layer has a refractive index of about 1.45.

6. The method according to claim 1, wherein the middle layer comprises at least about 50 mol% of the oxide of cerium.

7. The method according to claim 1, wherein at least one of the inner layer, the middle layer and the outer layer is sol-gel derived.

8. The method according to claim 1, wherein the heat treating in step (d) comprises tempering or bending.

9. The method according to claim 1, wherein the middle layer comprises a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of nickel, titanium, tantalum, hafnium, silicon and zirconium.

10. A method for producing a stress-resistant heat-treated anti-reflection coated inorganic substrate comprising:

(a) providing to an inorganic substrate a coating having a refractive index of at least about 1.90 comprising a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of silicon, nickel and transition metals of Group IIIB, Group IVB, Group VB and Group VIB of the Periodic Table, and

(b) heat treating the coated inorganic substrate;

wherein the heat-treated anti-reflection coated inorganic substrate is resistant to cracking and crazing.

11. The method according to claim 10, wherein the coating has a refractive index of at least about 2.0.

12. The method according to claim 10, wherein the coating comprises at least about 50 mol% of the oxide of cerium.

13. The method according to claim 10, wherein the coating is sol-gel derived.

14. The method according to claim 10, wherein the heat treating in step (b) comprises tempering or bending.

15. The method according to claim 10, wherein the coating comprises a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of nickel, titanium, tantalum, hafnium, silicon and zirconium.

16. A method for producing a stress-resistant heat-treated sol-gel derived thin film anti-reflection optical coating on an inorganic substrate comprising:

(a) immersing an inorganic substrate in an M solution comprising tetraethylorthosilicate and the reaction product of $TiCl_4$ and ethanol;

(b) withdrawing the substrate from the M solution to provide the substrate with a coating of the M solution;

(c) heat treating the substrate to form a silicon dioxide and TiO_2 layer having a refractive index of about 1.60 to about 1.90;

(d) immersing the substrate in an H solution comprising cerium nitrate hexahydrate, tetraethylorthosilicate and at least one compound of at least one transition metal of Group IIIB, Group IVB, Group VB or Group VIB of the Periodic Table;

(e) withdrawing the substrate from the H solution to provide the substrate with a coating of the H solution;

(f) heat treating the substrate to form an oxide layer having a refractive index of at least about 1.9;

(g) immersing the substrate in an L solution comprising tetraethylorthosilicate, ethanol and water;

(h) withdrawing the substrate from the L solution to provide the substrate with a coating of the L solution; and

(i) heat treating the substrate to form an oxide layer having a refractive index of about 1.45 and to form the optical coating;

wherein the heat-treated sol-gel derived thin film anti-reflection optical coating is resistant to cracking or crazing.

17. The method according to claim 16, wherein the oxide layer in step (f) has a refractive index of at least about 2.0.

18. The method according to claim 16, wherein the at least one transition metal in step (d) is selected from the group consisting of titanium, tantalum, hafnium, and zirconium.

19. The method according to claim 16, wherein the mixture in step (d) comprises at least about 50 mol% cerium nitrate heaxahydrate.

20. A method of making an article comprising bent glass comprising:

(a) coating a glass substrate with an inner layer comprising an oxide of titanium and an oxide of silicon;

(b) coating the inner layer with a middle layer comprising a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of silicon, nickel and transition metals of Group IIIB, Group IVB, Group VB and Group VIB of the Periodic Table;

(c) coating the middle layer with an outer layer comprising an oxide of silicon to form a coated glass substrate;

(d) bending the coated glass substrate; and

(e) making an article comprising the coated glass substrate;

wherein the article comprising bent glass is resistant to cracking or crazing.

21. The method according to claim 20, wherein the glass substrate is selected from the group consisting of soda lime float glass, borosilicate glass and quartz.

22. The method according to claim 20, wherein the inner layer has a refractive index of about 1.60 to about 1.90.

23. The method according to claim 20, wherein the middle layer has a refractive index of at least about 1.90.

24. The method according to claim 20, wherein the middle layer has a refractive index of at least about 2.0.

25. The method according to claim 20, wherein the outer layer has a refractive index of about 1.45.

26. The method according to claim 20, wherein the middle layer comprises at least about 50 mol% of the oxide of cerium.

27. The method according to claim 20, wherein the middle layer comprises a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of nickel, titanium, tantalum, hafnium, silicon, and zirconium.

28. The method according to claim 20, wherein the article comprises a display case.

29. The method according to claim 20, wherein at least one of the inner layer, the middle layer and the outer layer is sol-gel derived.

30. The method according to claim 20, wherein step (a) comprises:

(i) immersing the substrate in an M solution comprising tetraethylorthosilicate and the reaction product of $TiCl_4$ and ethanol;

(ii) withdrawing the substrate from the M solution to provide the substrate with a coating of the M solution; and

(iii) heat treating the substrate to form a silicon dioxide and TiO_2 layer having a refractive index of about 1.60 to about1.90.

31. The method according to claim 20, wherein step (b) comprises:

(i) immersing the substrate in an H solution comprising cerium nitrate hexahydrate, tetraethylorthosilicate and at least one compound of at least one transition metal of Group IIIB, Group IVB, Group VB or Group VIB of the Periodic Table;

(ii) withdrawing the substrate from the H solution to provide the substrate with a coating of the H solution; and

(iii) heat treating the substrate to form an oxide layer having a refractive index of at least about 1.9;

32. The method according to claim 20, wherein step (c) comprises:

(i) immersing the substrate in an L solution comprising tetraethylorthosilicate, ethanol and water;

(ii) withdrawing the substrate from the L solution to provide the substrate with a coating of the L solution; and

(iii) heat treating the substrate to form an oxide layer having a refractive index of about 1.45.

33. A method of improving crack resistance in a heat treated inorganic substrate comprising:

(a) providing to an inorganic substrate a coating having a refractive index of at least about 1.90 comprising a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of silicon, nickel and transition metals of Group IIIB, Group IVB, Group VB and Group VIB of the Periodic Table; and

(b) heat treating the coated substrate.

34. The method according to claim 33, wherein the coating has a refractive index of at least about 2.0.

35. The method according to claim 33, wherein the coating comprises at least about 50 mol% of the oxide of cerium.

36. The method according to claim 33, wherein the coating is sol-gel derived.

37. The method according to claim 33, wherein the heat treating comprises tempering or bending.

38. The method according to claim 33, wherein the coating comprises a mixture of an oxide of cerium and at least one oxide of a metal selected from the group consisting of nickel, titanium, tantalum, hafnium, silicon and zirconium.